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SYNTHESIS OF OXYARYLENE BBB POLYMERS

*POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION*

JUNE 1975

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Prepared for
AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "Synthesis of Novel Polymer Materials for High Temperature Resin Application." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F.E. Arnold as the Project Scientist.

This report has been reviewed by the Information Office (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


F. E. ARNOLD
Project Scientist

FOR THE COMMANDER


R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

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The resulting BBB type polymers with an increased number of rotational sites along the polymer backbone were soluble in m-cresol and exhibited glass transition temperatures in the 300°-350°C range. All of the polymers displayed good thermal and thermal oxidative stabilities characteristic of this class of materials.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "Synthesis of Novel Polymer Materials for High Temperature Resin Application." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFML Project Scientist. This report describes work conducted from March 1973 to December 1973.

The work described in this report was conducted in the Polymer Branch Laboratory by Dr. F. E. Arnold. The manuscript was released by the author in October 1974 for publication as a technical report.

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SUMMARY

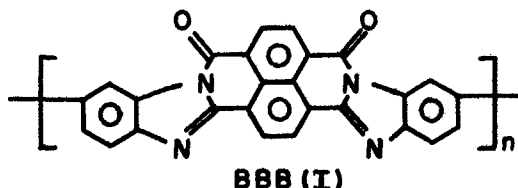
This work was performed to determine the extent to which processability parameters such as solubility and fusibility could synthetically be altered in the benzimidazobenzophenanthroline (BBB) polymer system. The BBB polymer has excellent thermal and thermal oxidative properties; however, the polymer is infusible and is only soluble in highly corrosive solvents.

A series of BBB polymers has been synthesized by the reaction of 1,4,5,8-naphthalenetetracarboxylic acid anhydride with oxyarylene tetraamines. The resulting BB-type polymers with an increased number of rotational sites along the polymer backbone were soluble in m-cresol and exhibited glass transition temperatures in the 300°-350°C range. All of the polymers displayed good thermal and thermal oxidative stabilities characteristic of this class of materials.

SECTION I

INTRODUCTION

During the past decade, the advent and development of aromatic heterocyclic polymers have constituted a very active part of high-temperature materials research. Poly(6,9-dihydro-6,9-dioxobisbenzimidazo [2,1-b:1',-2'-j]benzo[lmn]phenanthroline-3,12-diyl), referred to as BBB (1), is one of the most thermally stable aromatic heterocyclic polymers now known. First prepared in our laboratory (References 1 and 2), BBB has been developed (References 3 and 4) into a fibrous material showing excellent properties for deployable aerodynamic decelerators. The polymer has been studied extensively with respect to its synthesis



(Reference 5), thermal degradation (Reference 6), thermal oxidative degradation (Reference 7), molecular weight (Reference 8), glass transitions (Reference 9), and solution properties (Reference 10). The BBB polymer represents the state of art material in the field of aromatic heterocyclic polymer chemistry.

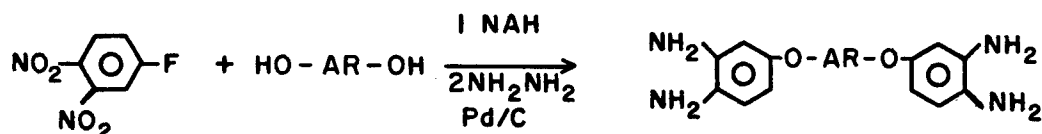
Although BBB is under development as a fibrous material, it has not as yet been successfully evaluated as a high temperature coating, adhesive, and composite material. A difficulty encountered with BBB and other highly fused aromatic heterocyclic polymers is that they are not soluble in conventional organic solvents nor do they exhibit glass transition temperatures by which they can be fabricated. BBB exhibits no glass transition temperature below its decomposition temperature and is soluble in only highly corrosive solvents such as sulfuric, chlorosulfonic, and methanesulfonic acids.

The objective of this work is to synthesize BB-type polymers with an increased number of rotational sites along the polymer backbone. The purpose of the work is to determine if the increase in rotational sites would provide materials with lower glass transition temperatures and improved solubility characteristics.

SECTION II

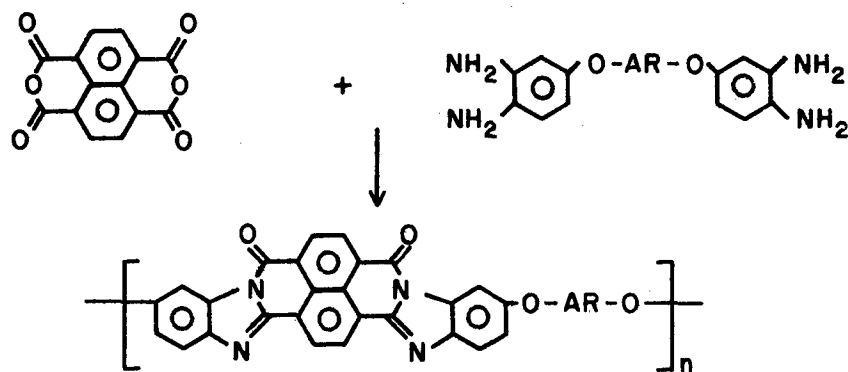
RESULTS AND DISCUSSION

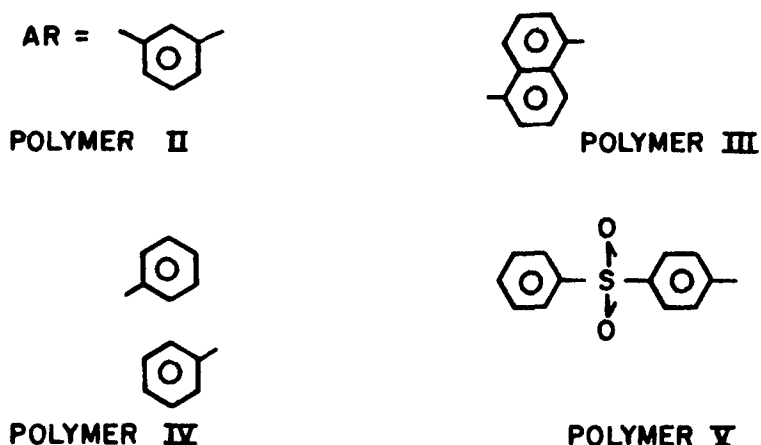
The BBB polymer is prepared by the solution polycondensation of 1,4,5,8-naphthalenetetracarboxylic acid or dianhydride and 3,3'-diaminobenzidine in polyphosphoric acid. In an effort to provide rotational sites along the polymer backbone, oxyarylene tetraamine monomers were used in place of 3,3'-diaminobenzidine. The experimental procedures for the new tetraamine monomers were provided by Major F. W. Villaescusa and Captain J. G. Breland Jr. of the Frank J. Seiler Research Laboratory, Colorado. The synthetic route used involved the nucleophilic substitution of various aryl diols with



4-fluoro-1,2-dinitrobenzene followed by reduction with hydrazine and palladium on carbon catalyst.

Four different oxyarylene tetraamines (Table I) were condensed with 1,4,5,8-naphthalenetetracarboxylic acid dianhydride to give polymers II, III, IV, and V.



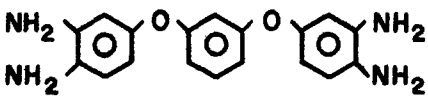
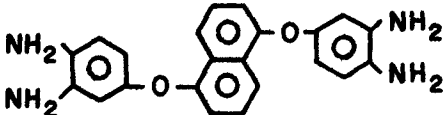
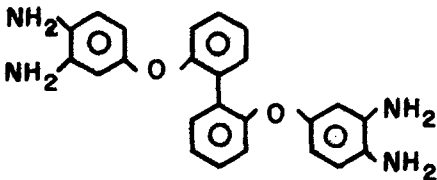
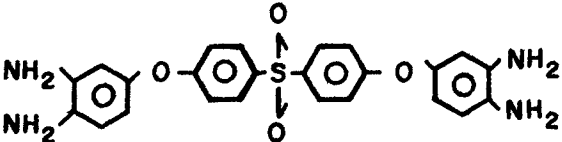


the polymerizations were carried out in deoxygenated polyphosphoric acid (PPA) at 180-195°C. The polymers were isolated by precipitation into anhydrous methanol, and purified by reprecipitation from methanesulfonic acid. Prior to obtaining the thermoanalytical properties of the polymers, they were endcapped with ortho-phenylenediamine at 180°C in PPA. Endcapping the polymers assured that endgroups would not detract from the thermogravimetric and thermomechanical analysis.

The polymers were completely soluble in m-cresol and all exhibited a glass transition temperature (T_g) below their decomposition temperature. A tabulation of viscosity and T_g data is given in Table II for polymers II-V. It can be seen from Table I that doubling the rotational sites along the polymer backbone from two for BBB, to four for polymer II substantially lowers the T_g . Further, increasing the rotational sites from four to six for polymer V shows a very small decrease in T_g .

The thermal properties for the polymers were quite good as shown by thermogravimetric analysis (Figures 1-4). Weight losses of five to ten percent, usually considered to be catastrophic, were not seen to occur for the polymers up to 600 to 650°C in nitrogen and 450 to 500°C in air. This is not surprising since the BBB polymer has been shown to exhibit excellent thermal properties.

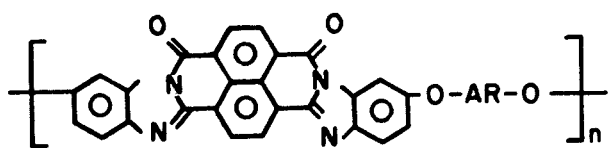

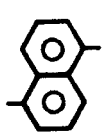
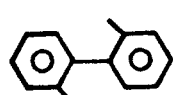
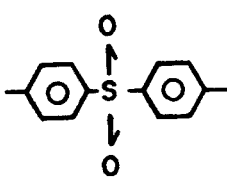
TABLE I
TETRAAMINE MONOMERS

Structure	MP.(°C)
	232-6°C ^a
	230-231°C
	172-174°C
	105-110°C

a. Melting point of tetrahydrochloride.

TABLE II

GLASS TRANSITION TEMPERATURE OF BENZIMIDAZOBENZOPHEN-
ANTHROLINE POLYMERS CONTAINING OXYARYLENE GROUPS

			
AR	POLYMER	$[\eta]^a$	T _g
Nil.	I (BBB)	1.5	550 ^b
	LL	0.80	325 ^b
	III	0.33	308 ^c
	IV	0.41	310 ^c
	V	0.56	294 ^c

a. Intrinsic viscosities determined in methanesulfonic acid.

b. Determined by TBA.

c. Determined by TMA.

SECTION III

EXPERIMENTAL

1. MONOMERS

a. The oxyarylenetetraamines (Table I) were first prepared by Major F. W. Villaescusa and Captain J. G. Breland Jr. The synthesis of the monomers will be the subject of a F.J.S.R.L. technical report.

b. 1,4,5,8-Naphthalenetetracarboxylic acid dianhydride (Celanese Research Company) was analyzed and used as received.

2. POLYMERS

Poly[6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',-2'-j]benzo[lmn]-[3,8]phenanthroline-3,12-diyl)oxy-m-phenylene-oxy]II

A mixture of 0.9904 g (3.25 mmoles) of 1,4,5,8-naphthalene-tetracarboxylic acid dianhydride and 1.524 g (3.25 mmoles) of 1,3-bis-(3,4-diaminophenoxy)benzene hydrochloride was added to 100 ml of deoxygenated polyphosphoric acid at room temperature. The mixture was heated under a nitrogen atmosphere to 75°C and maintained there for a period of eight hours. Then the temperature was gradually increased to 180°C and maintained there for ten hours. The product was obtained by pouring the cooled reaction mixture into one liter of well stirred methanol. After separating the precipitated product by filtration, the product was thoroughly washed with boiling methanol and dried at 80°C under reduced pressure for 24 hours to give 1.59 g (95%) of reddish brown polymer. The polymer product had an intrinsic viscosity $[\eta]$ of 0.8 as determined in methanesulfonic acid.

Analysis - Calc'd for $(C_{32}H_{14}N_4O_4)_n$: C, 74.13; H, 2.72; N, 10.80

Found: C, 73.73; H, 2.50; N, 10.30

Poly[6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',-2'-j]benzo[lmn]-[3,8]phenanthroline-3,12-diyl)oxy-1,5-naphthalene-oxy]III

A mixture of 0.4289 g (1.59 mmoles) 1,4,5,8-naphthalenetetracarboxylic acid dianhydride and 0.9957 g (1.59 mmoles) of 1,5-bis-(3,4-diaminophenoxy)naphthalene was added to 75 g of antimony trichloride. The mixture was slowly heated to 70°C, under a nitrogen atmosphere, where the antimony trichloride melted and the reaction mixture became

homogeneous. The reaction temperature was increased to 160°C and maintained at that temperature for six hours. Acetic acid was added to the cooled reaction mixture, thereby precipitating the product as a fine brown solid. After separating the product by filtration, it was washed with boiling acetic acid, methylene chloride, and methanol. The polymer, 0.9 g (100%), had an intrinsic viscosity of 0.4 as determined in methanesulfonic acid.

Analysis - Calc'd for $(C_{36}H_{16}N_4O_5)_n$: C, 76.05; H, 2.83; N, 9.86
 Found: C, 75.43; H, 2.46; N, 9.25

Poly[6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',-2'-j]benzo[1mn]-[3,8]phenanthroline-3,12-diyl)oxy-1,1'-biphenyl-oxy]IV

A mixture of 0.960 g (1.25 mmoles) of 2,2'-bis(3,4-diaminophenoxy)biphenyl and 0.343 g (1.27 mmoles) of 1,4,5,8-naphthalenecarboxylic acid dianhydride was added to 100 ml of deoxygenated polyphosphoric acid at room temperature. The mixture was slowly heated (8°C/min) under nitrogen to 195°C and maintained at that temperature for ten hours. The product was obtained by pouring the cooled reaction mixture into one liter of well stirred methanol. After isolating the product by filtration, it was thoroughly washed with anhydrous methanol and dried at 80°C under reduced pressure to give 0.75 g (100%) of reddish brown polymer. The polymer had an intrinsic viscosity of 0.41 as determined in methane-sulfonic acid.

Analysis - Calc'd for $(C_{38}H_{18}O_4N_4)_n$: C, 76.76; H, 3.05; N, 9.42
 Found: C, 79.43; H, 2.58; N, 8.91

Poly[6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',-2'-j]benzo[1mn]-[3,8]phenanthroline-3,12-diyl)oxy-4,4'-diphenylsulfide-oxy]V

4,4'-Di(3,4-diaminophenoxy)diphenyl sulfone (0.93 g, 2.08 mmoles) and 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (0.5585 g, 2.08 mmoles) were added to 100 ml of deoxygenated polyphosphoric acid. The mixture was slowly heated (8°C/min), under nitrogen, to 195°C and maintained at this temperature for ten hours. The reaction mixture was cooled to room temperature and poured into two liters of water, thereby precipitating the product. After separating the product by filtration, it was thoroughly washed with water and dried at 80°C under reduced pressure for 12 hours to give 1.28 g (94%) of a brown polymer. The

polymer had an intrinsic viscosity of 0.56 as determined in methanesulfonic acid.

Analysis - Calc'd for $(C_{38}H_{18}O_6N_4S)_n$: C,69.29; H,2.75; N,8.50

Found: C,67.50; H,2.25; N,8.01

3. POLYMER ENDCAPPING

To 100 g of deoxygenated PPA were added 0.5 g of polymer and 2 g of o-phenylenediamine. The solution was slowly heated (4°/min) to 180°C and 2 g of additional o-phenylenediamine was added. After eight hours at 180°C, the mixture was cooled to room temperature and precipitated into two liters of anhydrous methanol. The finely divided precipitated material was washed with methanol and dried under reduced pressure (0.40 mm).

CONCLUSIONS

This work was performed to determine the extent to which the processability and certain physical properties such as solubility and Tg could synthetically be altered. It has been shown that increasing the number of rotational sites along the BBB backbone renders the polymer soluble in m-cresol, a solvent which has been used in the fabrication of polyphenylquinoxalines. Increasing the number of rotational sites also decreases the Tg of the BBB from $> 550^{\circ}\text{C}$ to the $300\text{-}350^{\circ}\text{C}$ range. The results are positive and encouraging, although it is recognized that future work will be required to define more clearly the possible potential of such systems for Air Force use.

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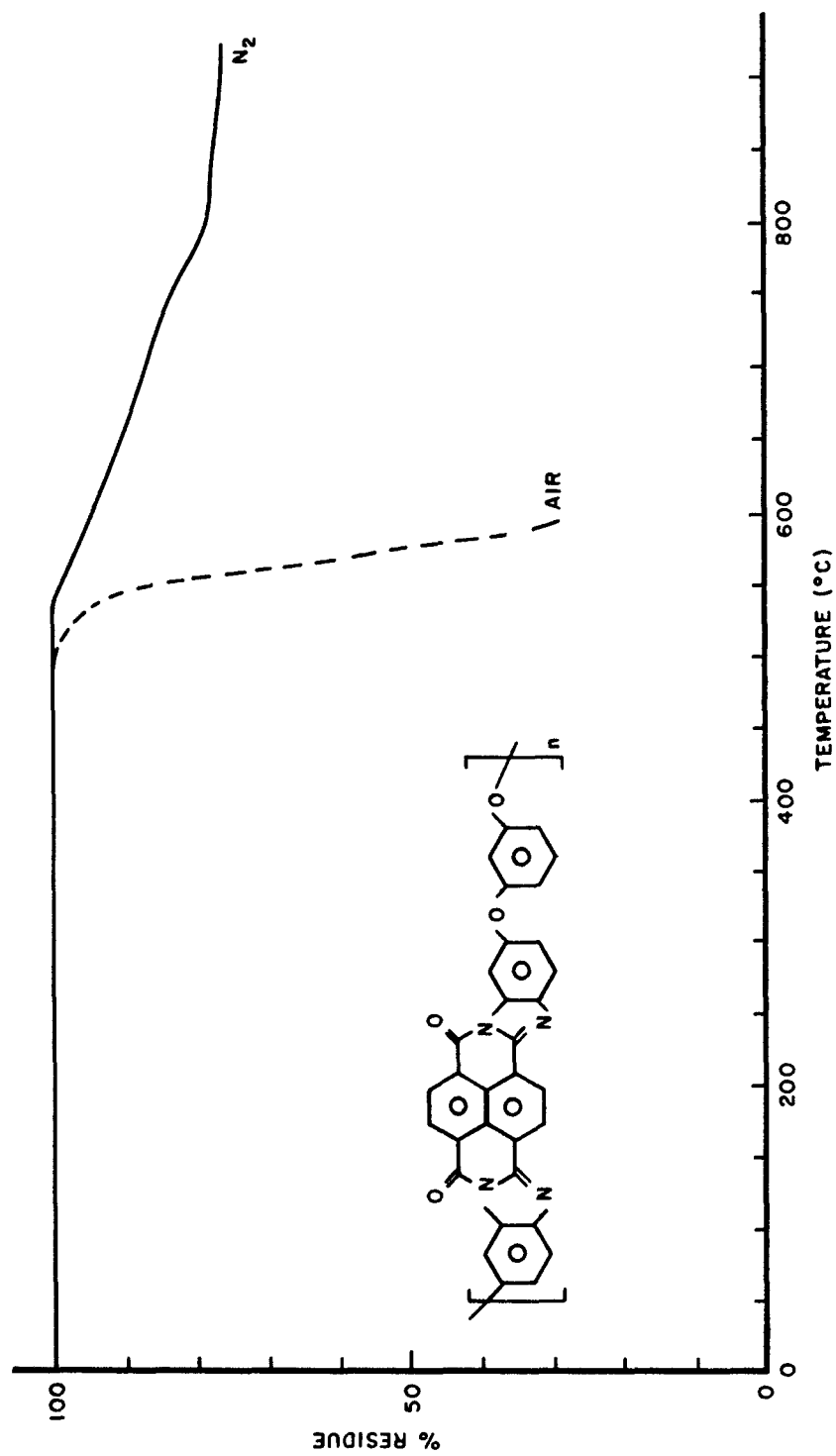


Figure 1. TGA of Poly[6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',-2'-j]benzo[1mn]-[3,8]phenanthroline-3,12-diyl)oxy-m-phenylene-oxy]n

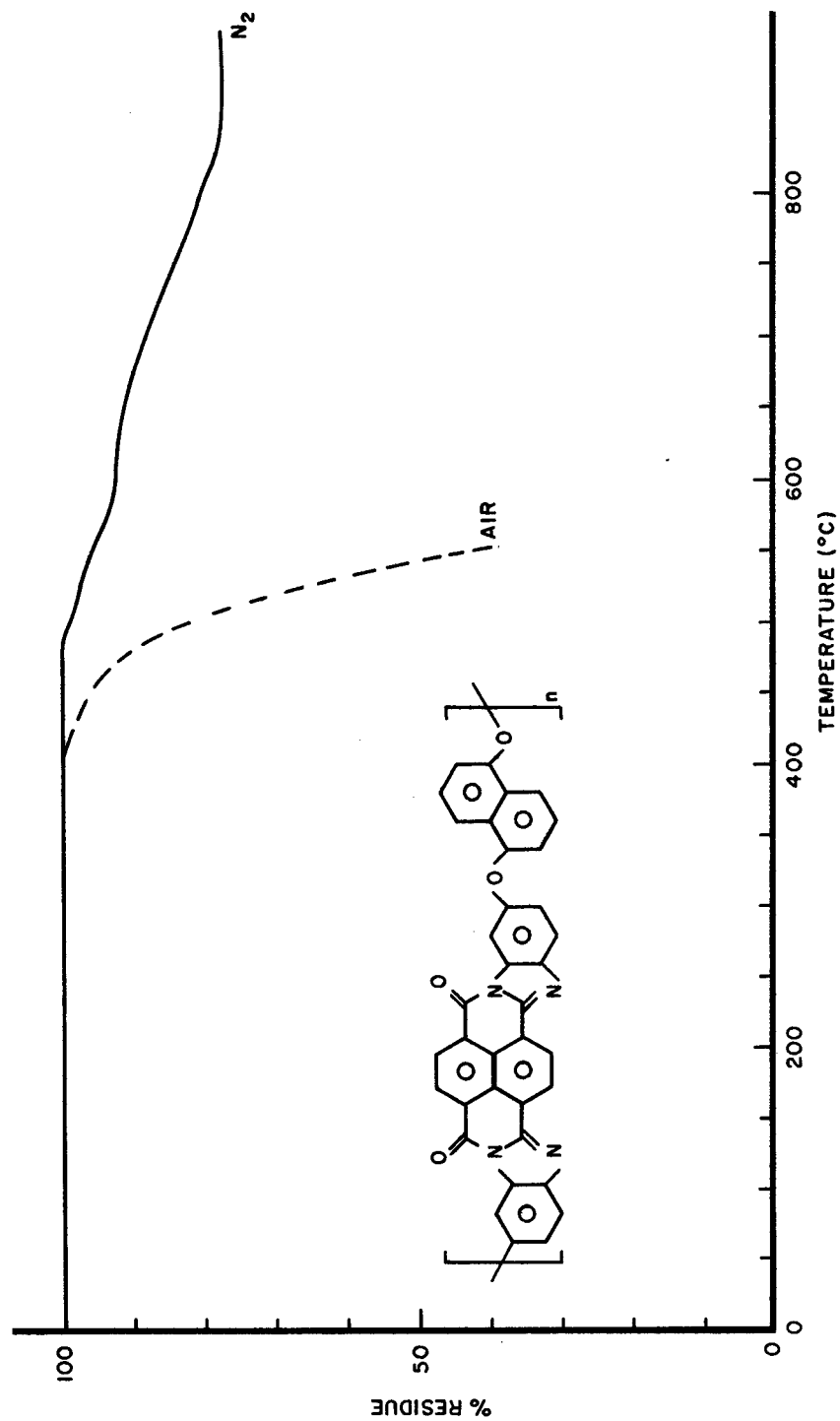


Figure 2. TGA of Poly[6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',2'-j]benzo[1mn]-[3,8]phenanthroline-3,12-diyl)oxy-1,5-naphthalene-oxyl]III

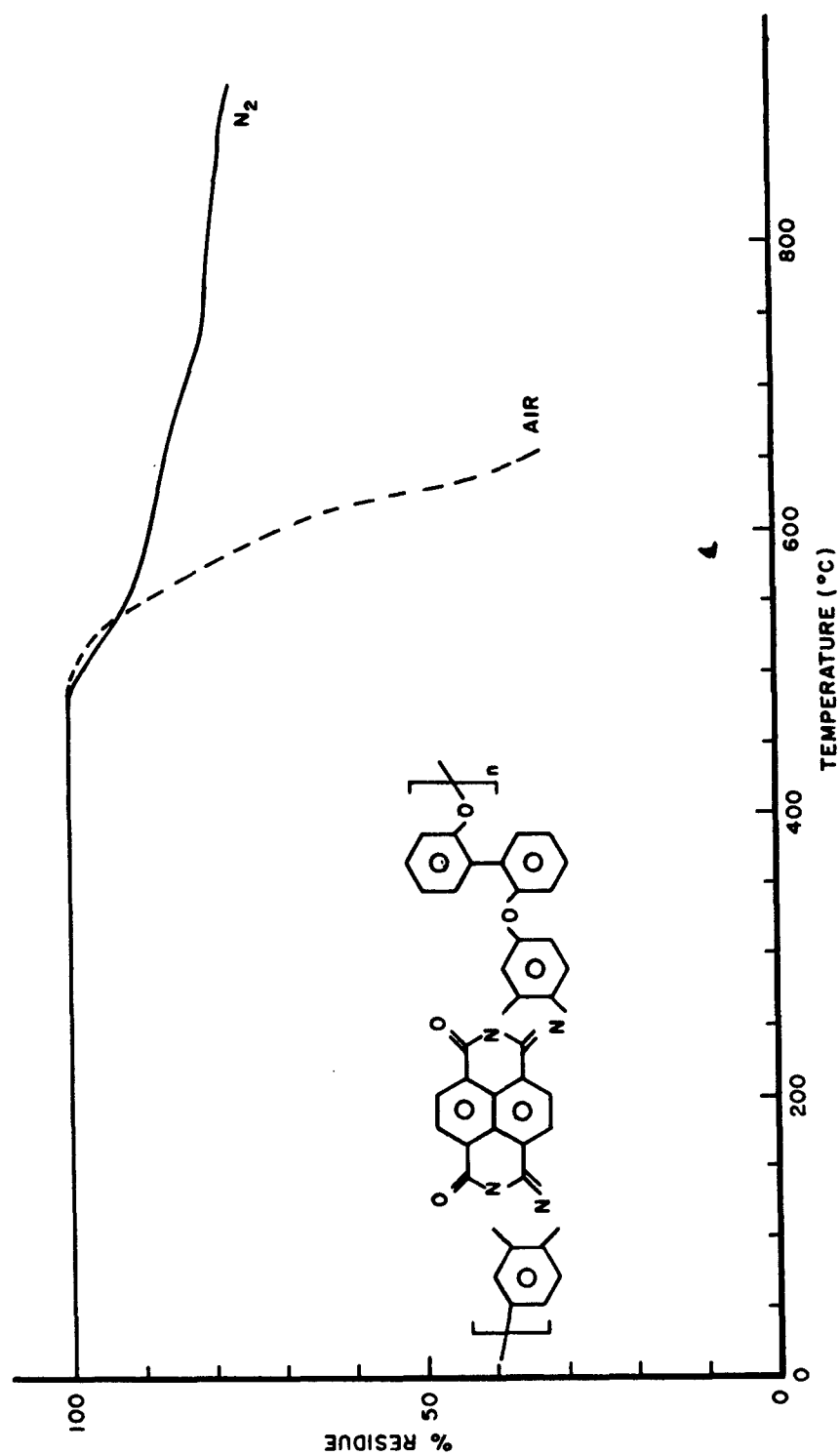


Figure 3. TGA of Poly[6,9-dihydro-6,9-dioxobenzimidazo[2,1-b:1',-2'-j]benzo[3,8]phenanthroline-3,12-diyl]oxy-1-1'-biphenyl-4-yl]IV

